PROCESS OPTIONS FOR EXTINCTION RECYCLE CONVERSION OF HEAVY OILS IN CATALYTIC TWO STAGE LIQUEFACTION

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ABSTRACT

Hydrocarbon Research, Inc. (HRI) is developing a Catalytic Two-Stage Liquefaction (CTSL) Process which converts coal to distillate liquid products. A particularly attractive feature of the process that has been demonstrated recently using two bituminous coal feedstocks (Illinois No. 6 and Ohio No. 5/6 coals) is the capability to achieve extinction conversion of heavy oil products (heavy vacuum distillate and soluble residuum oil) through integration of coal cleaning, product solids separation, and selective recycle. Yields of distillate oils of up to five barrels per M.A.F. ton of coal have been achieved. Elimination of heavy oils of boiling points above 700-750°F greatly simplifies downstream processing requirements. Several process configuration options and the resulting yield distributions are discussed.

INTRODUCTION

Hydrocarbon Research, Inc.'s (HRI) Catalytic Two-Stage Liquefaction (CTSL) Process features two close-coupled catalytic ebullated-bed reactor stages in series, with the first stage at a lower temperature than the second stage, so as to optimize the hydrogenation/conversion functions of the two stages. The process has been under development, sponsored by the U. S. Department of Energy (DOE), since 1982. This paper summarizes the status of the program and discusses the results of the most recent operations in HRI's continuously operated bench-scale unit which demonstrated extended operations with virtually complete elimination of residual oil and/or heavy vacuum gas oils from the net products of the operation. Upgrading studies by Chevron[1] have correlated upgrading costs directly with product oil end points and emphasized the need to eliminate the heavy vacuum gas oil products. Recently completed economic studies by HRI have shown a product cost benefit for the extinction mode of operation.[2] Such modes of operation were demonstrated for Illinois No. 6 and Ohio No. 5/6 bituminous coals.

PROCESS DESCRIPTION

The key feature which distinguishes the CTSL Process from other single- or two-stage liquefaction processes is the use of a relatively low temperature (<800°F) in the first-stage reactor which contains an effective hydrogenation catalyst. In this stage, coal is largely converted at a controlled rate by dissolution in the recycle solvent, allowing catalytic hydrogenation reactions, necessary to maintain solvent hydrogen-transfer capability and stabilize the liquefaction products, to keep pace with the rate of coal conversion. The second stage operates at more severe conditions, but not as severe as required in a single-stage mode such as in the H-Coal® Process, and it completes the job of coal conversion with the additional conversion of high boiling primary liquefaction products to high quality distillates. Overall, the CTSL Process obtains higher yields of better quality distillate products than obtained in competing technologies.

BENCH UNIT DESCRIPTION

Process development studies have been conducted in HRI's continuously operating two-stage Bench Unit, schematically shown in Figure 1. The operation is sustained with the net feed of only coal and hydrogen, with recycled solvent recovered from the contemporary gross products leaving the reaction system, by the distillation and filtration means indicated in Figure 1. The immediate recovery and recycle of solvent is a true prototype of full scale operations and facilitates the interpretation of the operating results, by avoiding the problems of batch and once-through experimental modes. There is an on-line sampling system for the slurry leaving the first stage, so that the effectiveness of each of the two stages can be assessed.

An important factor in process performance is the nature of the solvent that is recycled. Figure 1 includes a schematic summary of the modes of adjusting solvent composition. First, slurry product from the reaction system is distilled at atmospheric pressure to eliminate from the solvent pool middle distillate oils for which there is little incentive to submit to further processing by recycling to the liquefaction reactors. The atmospheric bottoms slurry can be recycled directly or further modified for recycle, either by a solids removal method, here pressure filtration although alternative methods are feasible, or by vacuum distillation which provides heavy vacuum distillate for incorporation in the recycle solvent pool. In the bottoms extinction demonstration operation summarized in this report, the atmospheric still was operated with a stripping gas to give a middle distillate endpoint (atmospheric still overhead going to product pool) and solvent pool IBP such that the solvent pool was virtually completely eliminated by undergoing further secondary reactions in the liquefaction reactors.

Bench unit scale of operations during the development program has been approximately 50 pounds per day. Scale up of the results from reactor systems of this size to plant scale has proven satisfactory for the H-Oil® and H-Coal® Processes, which employ the ebullated-bed reactor system used in the CTSL Process. The bench unit operations use a single charge of catalyst which is used in an extended operation, up to thirty days in some cases, without augmentation. This is in contrast with anticipated application to plant scale where, because of the convenience of the ebullated-bed system, a portion of the catalyst is to be replaced on a daily basis, so as to maintain a constant catalytic performance, while holding the reactors at a fixed temperature. Again, the interpretation of the bench scale results in projection of the amount of catalyst replacement required on a plant scale has proven to be satisfactory. The catalyst used in the operation described in this report is a commercially available hydrodesulfurization catalyst, one of several which have performed equally well.

DEMONSTRATION RUN PARAMETERS

The bottoms extinction operations showed that a sustained operation could maintain a product distribution eliminating the highest boiling constituents from the product pool. This mode requires that all such materials leaving the reactor be recycled to the reactor system. A portion of these high boiling oils are mixed with product solids (unreacted coal and ash), in the filter cake for these operations, and for inclusion in the solvent recycle pool these oils must be separated from the solids. For these experiments the filter cake was washed with low-boiling aromatic solvent, and the extracted oils were returned to the solvent pool after distilling off the solvent. Since this solvent washing operation had some handling and processing inefficiencies, some of the solvent range material was not available for recycle and was rejected as a net product of the operation. The bottoms extinction objective is limited only by the engineering problems of the recovery for recycle of solvent range material.

To reduce the scale and cost of the solvent/solids separation operations it is desirable to process feed of relatively low ash content. To this end for the demonstration operation, the available mine-washed coal was further cleaned by heavy-media washing which reduced the ash content by approximately half. Table 1 gives, for Illinois coal, the analyses for the as-received mine-washed coal and the heavy-media washed coal used in the demonstration run. Table 2 gives these analyses for the Ohio coal. The CTSL results with heavy media washed coal are not appreciably different from those using mine-washed coal, as shown in Table 3 which compares the CTSL results for the two types of feed in process development operations using the same operating conditions. The principal difference in the results is 3% higher coal conversion with the heavy-media washed feed, with the increased conversion appearing as light and middle distillate product. This higher coal conversion is ascribed to the removal, along with the ash, of a portion of the most difficult to convert portion of the coal. The bottoms extinction mode is as feasible for the mine-washed feed as for the heavy-media-washed feed. The selection between these alternatives is an economic-engineering judgment involving the costs of product solids separation and the feasibility of alternative uses for the high ash reject from the heavy-media washing operation.

The vacuum gas oil extinction mode of operation consisted principally of unfiltered atmospheric still bottoms along with sufficient vacuum gas oil, obtained by vacuum distillation of the balance of the atmospheric still bottoms, to achieve extinction of the vacuum gas oil components. Here, too, the atmospheric still was operated with stripping gas to give a solvent pool IBP such that the vacuum gas oil component would be eliminated. Because of the reduction of the proportion of residual oil in the recycled solvent pool there would be a net production of residual oil from the operation, which would be withdrawn from the process as a vacuum bottoms slurry in combination with the unreacted coal and ash.

With the normal catalyst activity decline, operating conditions were adjusted so as to maintain the bottoms or gas oil extinction objectives. To this end, the temperatures of the two stages were increased progressively during the runs. Figure 2 summarizes the reactor temperature changes during the bottoms extinction demonstration run using Illinois No. 6 coal. Here, between the seventh day and the twenty-fifth day of the run, during which the bottoms extinction objectives of the run were attained (see below), the first-stage temperature was increased by 15°F and the second-stage temperature was increased by 20°F. Nominally, in a plant scale operation with daily replacement of catalyst, any level of performance obtained during the run could be maintained using the temperatures holding at that stage of the run and an appropriate rate of catalyst replacement that would maintain the catalyst activity holding for the particular stage of the operation. Also, during the run there was a progressive adjustment in the cut point between the atmospheric overhead withdrawn as product and the solvent recycle component being extincted, as summarized in Figure 3. This cut point was increased by about 80°F over the interval of the run during which the extinction objective was maintained. Nominally, such an adjustment of the cut point is not necessary to maintain the extinction objective, but without this adjustment in cut point greater changes in reactor temperatures would have been necessary in maintaining the extinction objective at a constant distillate product end point.

A comparison of the process options investigated highlighting the cut point differences is presented in Table 4.

OPERATING RESULTS WITH ILLINOIS COAL

The operating results for the demonstration operation in the bottoms extinction mode with Illinois coal are summarized in Table 5. The results are the average values for the seventh through twenty-fifth days of the run during which bottoms extinction objectives were maintained. Recycle solvent inventory corrections based on actual analysis were included. Figures 4 through 8 summarize day-by-day some details of the product distribution during the run, illustrating the degree to which minimum bottoms yields were maintained. Over this interval of the run, during which the endpoint of the atmospheric overhead product averaged 750°F, the yield of C_4-750°F distillate product averaged 77.2 W % of M.A.F. coal (corresponding to 5 barrels/ton of M.A.F. coal), with 1.0 W % yield of heavier distillates boiling to 975°F, and 2.7 W % yield of residual oil. Table 5 also summarizes the results of a comparable conventional CTSL operation with the heavy-media washed coal in which the 650-750°F boiling range material was included in the solvent recycle.[3,4] The change in the composition of the solvent recycle lowered the yield of 750°F$^+$ oils plus residuum from 19.6 W % of M.A.F. coal to 3.6 W %. Some of this change is due to the higher reactor temperatures used in the extinction mode operation, but other experimental work has shown that less than one-half of the difference is associated with the change in temperatures.

Figure 4 shows that the yield of C_4-End Point(about 750°F) product scattered around the average value during the seventh through twenty-fifth days of the run. Figure 5 displays a similar pattern for the 975°F$^+$ residual oil yield, and Figure 6 for the yield of heavy distillate to 975°F retained in the solvent recycle pool. Figure 7 shows an increase in coal conversion of about 1.5 W % over this interval of the run. Figure 8 shows an increase in C_1-C_3 hydrocarbon gas yield of about 2.5 W %.

OPERATING RESULTS WITH OHIO COAL

The operating results for the demonstration operations with Ohio No. 5/6 bituminous coal in the bottoms extinction mode and in the gas oil extinction mode are summarized in Table 6. These two types of operation were demonstrated in a single run, in which the bottoms extinction mode was used for the first ten days, and the vacuum gas oil extinction mode for the balance of the operations up to twenty-two days. The stage temperatures were progressively increased during these operations, similarly to the pattern used for the Illinois coal operations, with the reactor temperatures being increased by about 20°F over the interval of the run during which the extinction objectives were attained.

The bottoms extinction operation with Ohio coal maintained a 975°F$^+$ residual oil yield of 1.8 W % of M.A.F. coal. However, the yield of 750-975°F gas oil was somewhat higher, averaging 8.5 W %. Since there was virtually complete elimination of the 750-975°F fraction in the subsequent vacuum gas oil extinction operation, there is probably no barrier to equivalent extinction in the bottoms extinction mode. The shortfall in performance in this specific operation was probably due to too low a cut point between the atmospheric still overhead product and solvent recycle pool, at 700°F. It is probable that with this cut point raised by 25-50°F, there would have been essentially complete extinction of the 750°F$^+$ materials, with a total yield of C_4-750°F distillate product of about 77 W % of M.A.F. coal. This is similar to the yield in this mode of operation with Illinois coal. Beyond this consideration of the heavy gas oil extinction, the greatest difference from the Illinois coal results is about 2 W % higher yield of unconverted coal for the Ohio coal.

The vacuum gas oil extinction operation with Ohio coal gave a yield of 750-975°F gas oil of 0.2 W % of M.A.F. coal. For this operation, the yield of 975°F$^+$ residual oil was 14.1 W %, which would be taken off as a vacuum bottoms slurry along with the unreacted coal and ash. Such a slurry would have a composition of 61% residual oil, 21% unconverted coal, and 18% ash, and could be pumped for internal use as fuel or as raw material for hydrogen manufacture. The yield of C_4-750°F distillate was 65.1 W % of M.A.F. coal for this operation.

RESULTS AND CONCLUSIONS

- Heavy oil extinction recycle has been demonstrated for vacuum gas oil and vacuum gas plus residual oil for bituminous coals.
- Up to five barrels of distillate liquid product per ton of moisture ash free coal feed was produced. These yields are the highest demonstrated continuously for a direct liquefaction process.
- Increased liquid yields and reduced process separation costs were achieved through deep cleaning of bituminous feed coals.
- The distillate yields from Ohio coal are equivalent to those from Illinois coal at similar extinction recycle operating conditions.

ACKNOWLEDGEMENT

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REFERENCES

1. Sullivan, R. F., et al, "Transportation Fuels From Direct-Liquefaction Products". Division of Fuel Chemistry of the American Chemical Society, Anaheim, California, September 1986.

2. Abrams, L. M., A. G. Comolli, G. A. Popper, C. Wang and G. Wilson, "Catalytic Two-Stage Liquefaction Process - Illinois Coal Conceptual Commercial Plant Design and Economics". Department of Energy Topical Report prepared under Contract No. DE-AC22-85PC80002, to be issued February - March 1988.

3. McLean, J. B., A. G. Comolli, E. S. Johanson and T. O. Smith, "Demonstration Results for Illinois No. 6 Coal". DOE Direct Liquefaction Contractors' Conference, Pittsburgh, Pennsylvania, October 1987.

4. Comolli, A. G., E. S. Johanson, J. B. McLean and T. O. Smith, "Process Variable Studies and Residual Oil Extinction Recycle in Catalytic Two-Stage Liquefaction". DOE Direct Liquefaction Contractors' Review Meeting, Monroeville, Pennsylvania, October 1986.

TABLE 1

ILLINOIS COAL FEED ANALYSIS

SOURCE: ILLINOIS No. 6, BURNING STAR No. 2 MINE

	MINE-WASHED	HEAVY MEDIA CLEANED
PROXIMATE, W % DRY		
Fixed Carbon	51.5	54.1
Volatile Matter	38.2	40.4
Ash	10.3	5.5
ULTIMATE, W % DRY		
Carbon	70.4	73.9
Hydrogen	4.5	4.9
Nitrogen	1.4	1.5
Sulfur	3.6	2.8
Ash	10.6	5.8
Oxygen (Difference)	9.5	12.1
PETROGRAPHIC, V %		
Total Reactives	88.2	91.5
Total Inerts	11.8	8.5
Fusinite	1.9	0.3

TABLE 2

OHIO COAL FEED ANALYSIS

SOURCE: OHIO No. 5/6, CRAVAT COAL COMPANY

	MINE-WASHED	HEAVY MEDIA CLEANED
PROXIMATE, W % DRY		
Fixed Carbon	56.1	50.6
Volatile Matter	43.9	43.4
Ash	8.5	4.0
ULTIMATE, W % DRY		
Carbon	73.1	77.5
Hydrogen	4.8	5.0
Nitrogen	1.5	1.6
Sulfur	2.9	2.1
Ash	8.5	4.0
Oxygen (Difference)	9.2	9.8
PETROGRAPHIC, V %		
Total Reactives	88.0	90.4
Total Inerts	10.8	7.8
Fusinite	1.1	1.8

TABLE 3

OPERATING RESULTS BENCH UNIT CTSL OPERATIONS WITH MINE-WASHED AND HEAVY MEDIA WASHED ILLINOIS COAL

	WASHED	
COAL PREPARATION	Mine	Heavy-Media
ASH IN COAL FEED, W %	10.55	5.33
RUN	18	19
DAYS ON STREAM, Average	8	9
Reactor Temperatures, °F		
First Stage, Average	750	750
Second Stage, Average	810	810
End Point of Atmospheric Overhead Product, °F	670	664
PRODUCT DISTRIBUTION, W % OF M.A.F. COAL		
C_1-C_3 in Gases	5.9	6.2
C_4-390°F Naphtha	17.2	19.0
390-650°F Distillates	32.9	35.7
650-975°F Distillates	19.2	18.5
975°F$^+$ Residual Oil	8.3	8.3
Unconverted Coal	7.0	4.0
Water	11.7	11.7
H_2S, NH_3, CO_X	5.0	4.3
Total (100 + H_2 Reacted)	107.2	107.7
Total C_4-975°F	69.2	73.2
Distillate Yield Bbls/Ton	4.2	4.7

TABLE 4

COMPARISON OF PROCESS OPTIONS EVALUATED

	Product					
	Vacuum Gas-Oil	Residual Oil	Clean Coal	Solids Rejection	W % Distillate	Distillate End Point
Illinois No. 6 Coal Runs						
I-10/11 - Demonstration	Yes	Yes	No	VSB	60	975°F
I-13 - Process Variable	No	No	No	DS		
I-27 - Demonstration	No	No	Yes	DS	77	750°F
Ohio No. 5/6 Coal Runs						
0-1 - Demonstration	No	No	Yes	DS	70	700°F
	No	Yes	Yes	VSB	65	700°F

VSB = Vacuum Still Bottoms
DS = Dry Solids

TABLE 5

EXPERIMENTAL RESULTS OF CONVENTIONAL AND EXTINCTION MODES OF CTSL BENCH UNIT OPERATIONS WITH ILLINOIS COAL

MODE	CONVENTIONAL	EXTINCTION
RUN	19	27
DAYS ON STREAM, Average	14	16
Reactor Temperatures, °F		
First Stage, Average	750	761
Second Stage, Average	810	817
End Point of Atmospheric Overhead Product, °F	656	749
PRODUCT DISTRIBUTION, W % OF M.A.F. COAL		
C_1-C_3 Hydrocarbons	6.8	8.3
C_4-390°F Naphtha	18.9	20.3
390-650°F Distillates	32.4	37.5
650-750°F Distillates	9.1	19.5
C_4-750°F Distillates	60.4	77.3
750-975°F Distillates	11.0	1.0
975°F$^+$ Residual Oil	9.5	2.7
Unconverted Coal	3.8	3.3
Water	11.2	10.8
H_2S, NH_3, CO_X	4.6	4.2
Total (100 + H_2 Reacted)	107.3	107.6

TABLE 6

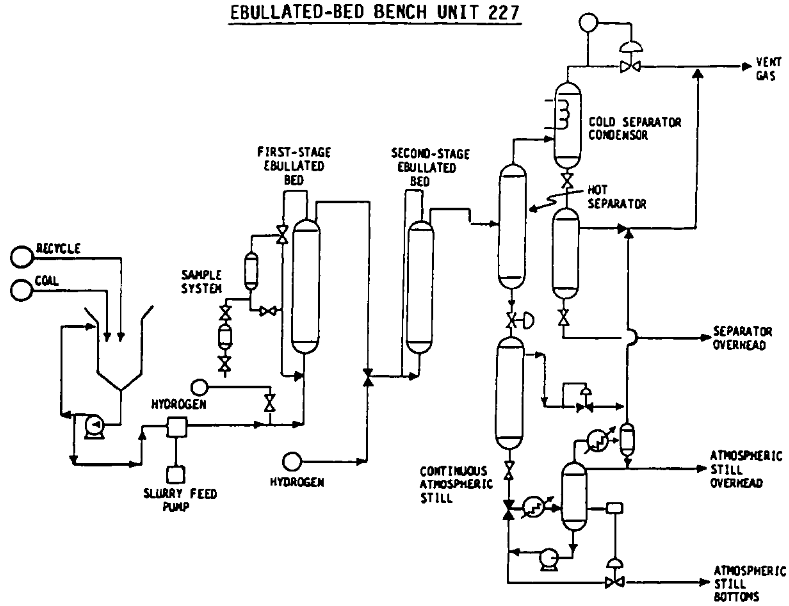
EXPERIMENTAL RESULTS OF BOTTOMS AND VACUUM GAS OIL EXTINCTION CTSL BENCH UNIT OPERATIONS WITH OHIO COAL

MODE	BOTTOMS EXTINCTION	VACUUM GAS OIL EXTINCTION
RUN	0-2	0-2
DAYS ON STREAM, Average	7	18
Reactor Temperatures, °F		
First Stage, Average	753	764
Second Stage, Average	806	819
End Point of Atmospheric Overhead Product, °F	702	697
End Point of Vacuum Gas Oil Product, °F	---	975
PRODUCT DISTRIBUTION, W % OF M.A.F. COAL		
C_1-C_3 in Gases	7.9	10.1
C_4-390°F Naphtha	19.1	18.8
390-650°F Distillates	36.8	38.1
650-975°F Distillates	14.6	8.1
C_4-750°F Distillates	70.5	65.1
750-975°F Gas Oil	8.5	0.3
975°F$^+$ Residual Oil	1.8	14.1
Unconverted Coal	5.2	4.8
Water	10.0	9.0
H_2S, NH_3, CO_X	3.5	3.4
Total (100 + H_2 Reacted)	107.4	106.7
Distillate Yield, Bbls/Ton	4.3	4.0

Note: $C_4$975°F Yield, 79% equal to 5:1 Bbls/Ton

FIGURE 1

EBULLATED-BED BENCH UNIT 227



BENCH UNIT - RECYCLE PROCEDURES

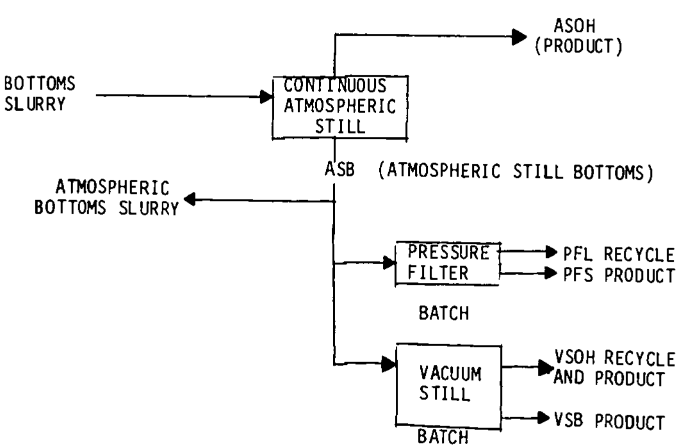


FIGURE 2

REACTOR TEMPERATURES

CTSL DEMONSTRATION OPERATION WITH ILLINOIS COAL

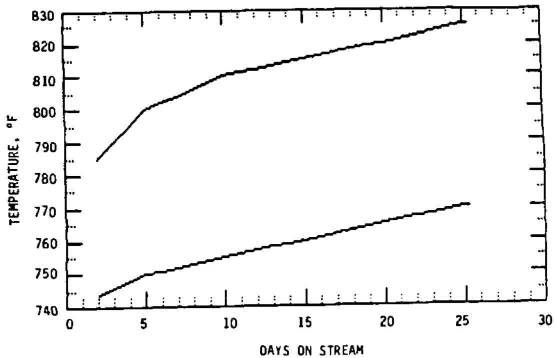


FIGURE 3

ATMOSPHERIC STILL CUT POINT

CTSL DEMONSTRATION OPERATION WITH ILLINOIS COAL

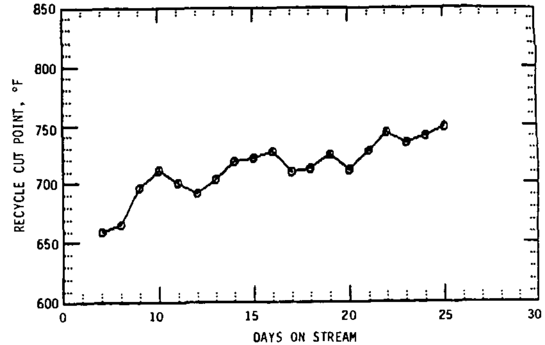


FIGURE 4

C_4-END POINT DISTILLATE YIELDS

CTSL DEMONSTRATION OPERATION WITH ILLINOIS COAL

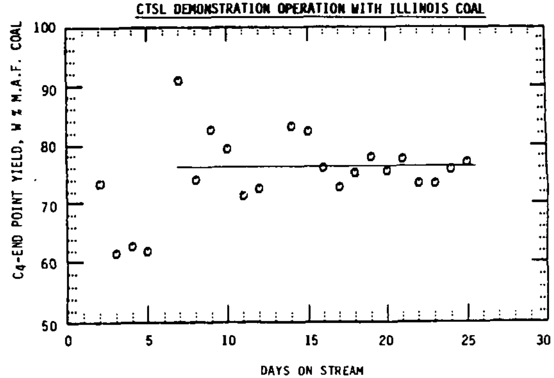


FIGURE 5

975°F+ YIELD

CTSL DEMONSTRATION OPERATION WITH ILLINOIS COAL

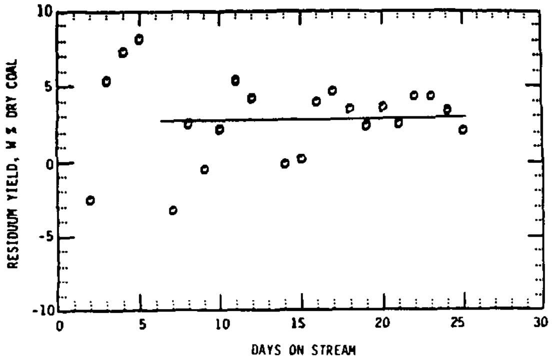


FIGURE 6

END POINT PLUS DISILLATE YIELD

CTSL DEMONSTRATION OPERATION WITH ILLINOIS COAL

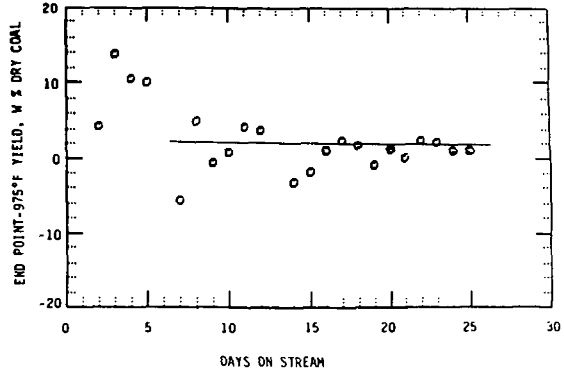


FIGURE 7

COAL CONVERSION

CTSL DEMONSTRATION OPERATION WITH ILLINOIS COAL

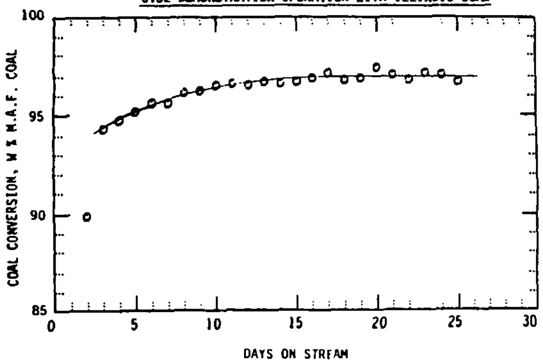


FIGURE 8

C_1-C_3 YIELDS

CTSL DEMONSTRATION OPERATION WITH ILLINOIS COAL